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Theoretical exploration of uranyl complexes of a designed polypyrrolic macrocycle: Structure/property effects of hinge size on Pacman-shaped complexes**

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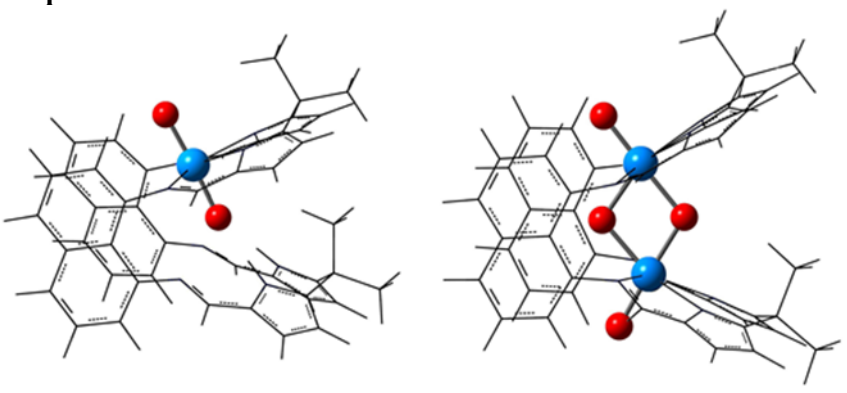
Supporting information:
[†]Electronic Supplementary Information (ESI) available: Figure of structures of mononuclear uranium complexes; figures of simulated vibrational spectra, and tables of geometry parameters and electronic information of mono- and binuclear uranium complexes; table of geometry parameters of the solvated mononuclear uranium complexes with the L2 macrocycle. See http://dx.doi.org/10.1039/C2DT31055D

Graphical abstract:



Synopsis:
A new Schiff-base calixpyrrole ligand with naphthalenyl linkers was predicted by relativistic density functional theory to provide a framework suited to the formation of mono- and binuclear U(VI) and U(V) dioxo complexes.

Abstract

A polypyrrolic macrocycle with naphthalenyl linkers between the N_4-donor compartments (L^2) was designed theoretically according to its experimentally-known analogues with phenylenyl (L^1) and anthracenyl (L^3) linkers. The uranyl and bis(uranyl) complexes formed by this L^2 ligand have been examined using scalar-relativistic density functional theory. The calculated structural properties of the mononuclear uranyl-L^2 complexes are similar to those of their L^1 counterparts. The binuclear L^2 complexes exhibit a butterfly-like bis(uranyl) core in which a linear uranyl is coordinated in a side-by-side fashion to a *cis*-uranyl unit. The calculated U=O bond orders in the uranyl-L^2 complexes indicate partial triple bonding character with the only exceptions being the U-O_{endo} bonds in the U_2O_4 core of the butterfly-shaped binuclear complexes. Overall, the bond orders agree with the trends in the calculated U=O stretching vibrational frequencies. Regarding the bis(uranyl) L^1, L^2 and L^3 complexes, the phenylenyl-hinge L^1 complexes adopt a butterfly-like and a T-shaped isomers in the oxidation state of U(VI), but only a butterfly-like one in the U(V), which differs from that of the naphthalenyl-hinge L^2 complexes as well as the lateral twisted structure of the anthracenyl-hinge L^3 complexes. The intramolecular cation-cation interactions are found in the L^1 and L^2 complexes, but are absent in the L^3 complexes. Finally, using model uranyl transfer reactions from the L^1 complexes, the formation of the mononuclear L^2 complexes is calculated to be a slightly endothermic process. This suggests that it should be possible to synthesize the L^2 complexes using similar protocols employed for the L^1 complexes.

Introduction

Polypyrrolic macrocycles such as porphyrins, expanded porphyrins, and calixpyrroles have been investigated as prospective agents for the complexation of transition metals and actinide cations.[1-6] Amongst them, the flexible Schiff-base calixpyrrole H_4L^1 (Chart 1), prepared independently by the Sessler[7] and Love[8] groups, acts as a ligand for the uranyl ion,[9] the most thermodynamically stable and the most prevalent form of uranium in the processing of nuclear fuel and waste.[10-16] The uranyl-L^1 complex adopts 'Pacman-like'[17-19] geometries in which one N_4-donor site is vacant. Significantly, this confined microenvironment has been found to engender new reactions of the uranyl oxo groups by favoring proximate reagents. For example, the strong U=O bonding in $[(UO_2)(THF)(H_2L^1)]$ can be disrupted by substituting the pyrrolic hydrogens in the vacant pocket with alkali metal ions such as lithium and potassium, transition metals, and the lanthanides, resulting, in some cases, in

pentavalent uranyl complexes, together with silylation and C-H activation reactions at the oxo group.[20-25]

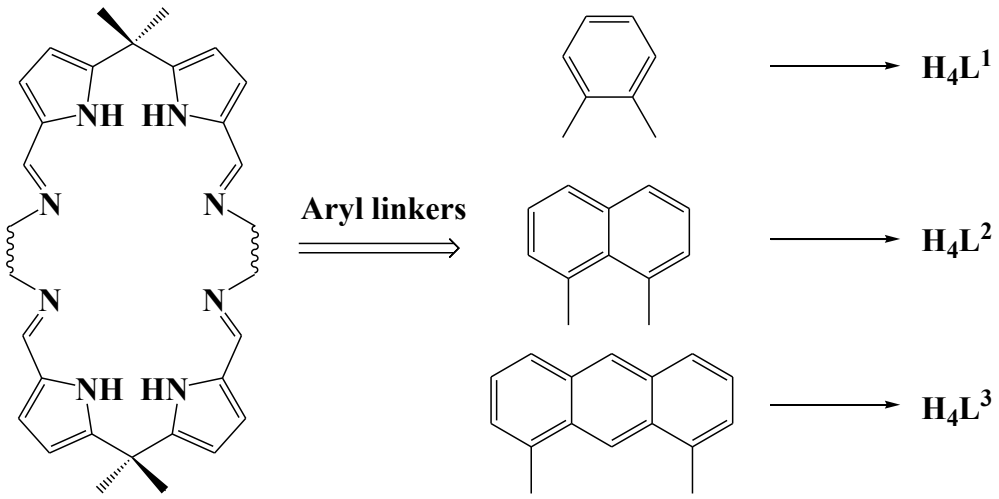


Chart 1. Polypyrrolic macrocycles with phenylenyl (H_4L^1), naphthalenyl (H_4L^2) and anthracenyl (H_4L^3) linkers.

Cation-cation interactions (CCI) were originally discovered in solutions of UO_2^{2+} and NpO_2^+ and[26] denotes the coordination of the oxo atom of one actinyl unit to the actinyl metal center of another.[27-36] These interactions play an important role in the actinyl chemistry of solution and solid state. For example, CCIs can lead to the formation of dimers,[26-31] oligomers,[35-37] one-dimensional chains and multi-dimensional networks[38-47] that do not necessarily require the support of ancillary ligands. CCIs are particularly well known for An(V) (An = U, Np and Pu),[29, 31-35, 48-50] but remain rare in U(VI) chemistry.[37-42]

Although initially only the mononuclear uranyl complex [$(UO_2)(THF)(H_2L^1)$] was obtained experimentally, our theoretical studies showed that H_4L^1 could potentially accommodate two uranyl ions to form two bis(uranyl) [$(U^{VI}O_2)_2(L^1)$] isomers,[51] labeled as $\mathbf{B}^{VI}L^1$ and $\mathbf{T}^{VI}L^1$ (Table 1), respectively, due to the butterfly-like and T-shaped structures resulting from CCIs. Upon reduction, only the butterfly-like complex ($\mathbf{B}^{V}L^1$) was predicted to be thermodynamically favorable in the subsequent calculations.[52] This prediction was recently supported experimentally with the report of the binuclear complex [$\{(Me_3Si)OU(\mu\text{-}O)\}(L^1)$] which contains two silylated pentavalent uranium oxo groups derived from two trans-uranyl cations.[24] Furthermore, we calculated that binuclear uranyl complexes of L^3 (Chart 1), a macrocycle similar to L^1 but with anthracenyl linkers between the two

N_4-donor compartments, are theoretically[53] and experimentally[54] accessible but do not exhibit intramolecular CCIs and oxo-group isomerization.

Table 1. The calculated complexes and their abbreviations.

Complexes	Abbreviation	Reference
Mononuclear $[(U^{VI}O_2)(H_2L^2)]$	$\mathbf{M}^{VI}L^2$	This work
Mononuclear $[(U^{V}O_2)(H_2L^2)]^-$	$\mathbf{M}^{V}L^2$	This work
Mononuclear $[(U^{VI}O_2)(py)(H_2L^2)]$	py$\mathbf{M}^{VI}L^2$	This work
Mononuclear $[(U^{V}O_2)(py)(H_2L^2)]^-$	py$\mathbf{M}^{V}L^2$	This work
Butterfly-typed $[(U^{VI}O_2)_2(L^2)]$	$\mathbf{B}^{VI}L^2$	This work
Butterfly-typed $[(U^{V}O_2)_2(L^2)]^{2-}$	$\mathbf{B}^{V}L^2$	This work
Mononuclear $[(U^{VI}O_2)(H_2L^1)]$	$\mathbf{M}^{VI}L^1$	This work
Mononuclear $[(U^{V}O_2)(H_2L^1)]^-$	$\mathbf{M}^{V}L^1$	This work
Butterfly-typed $[(U^{VI}O_2)_2(L^1)]$	$\mathbf{B}^{VI}L^1$	Ref. [51]
T-shaped $[(U^{VI}O_2)_2(L^1)]$	$\mathbf{T}^{VI}L^1$	Ref. [51]
Butterfly-typed $[(U^{V}O_2)_2(L^1)]^{2-}$	$\mathbf{B}^{V}L^1$	Ref. [52]
Mononuclear $[(U^{VI}O_2)(H_2L^3)]$	$\mathbf{M}^{VI}L^3$	Ref. [53]
Mononuclear $[(U^{V}O_2)(H_2L^3)]^-$	$\mathbf{M}^{V}L^3$	Ref. [53]
Non-CCIs $[(U^{VI}O_2)_2(L^3)]$	$\mathbf{N}^{VI}L^3$	Ref. [53]
Non-CCIs $[(U^{V}O_2)_2(L^3)]^{2-}$	$\mathbf{N}^{V}L^3$	Ref. [53]

It is clear from this previous work,[51, 53] and that for the analogous cofacial diporphyrins,[17, 55] that the relative separation of the two metal compartments moderates the structures and properties of the resulting complexes. Herein, we report the use of relativistic density functional theory (DFT) to explore theoretically the structural properties and reactions of mono- and binuclear uranyl complexes with the experimentally unknown Schiff-base macrocyclic ligand L^2 in which the two N_4-donor compartments are separated by a naphthalenyl linker in place of the previous phenyl or anthracenyl hinges.

Computational details

The structural and electronic properties of the uranyl complexes with the L^2 ligand (in Chart 1) have been investigated theoretically. We have also examined the effect of varying the number of uranyl

ions (one and two) as well as the uranium oxidation states (U^{VI} and U^{V}). In continuation of our previous studies on uranium complexes with the L^1 and L^3 ligands,[51-53] we compared the effects of hinge size in these Pacman-like uranium complexes (L^1, L^2 and L^3) on their structures, vibrational spectra and reaction properties. See Table 1 for the complexes and their abbreviations presented in this work.

Relativistic density functional theory with the PBE functional[56] was applied in these calculations. All geometry optimizations were accomplished with the Priroda code.[57-61] Priroda applies a scalar relativistic all-electron approach[62] that uses the full Dirac equation but with spin-orbit projected out and neglected.[63] All-electron correlation-consistent double-ς polarized quality basis sets were used for the large component, accompanied by the corresponding kinetically balanced basis sets for the small component.[59, 60] Subsequent analytical frequency calculations were used to confirm the nature of the stationary points on the potential energy surface and also to obtain vibrational frequencies and thermodynamic data. We simulated vibrational spectra of complexes using the Lorentzian function. Population-based Mayer[64] bond orders and atomic charges as developed by Hirshfeld[65] were calculated based on these PBE calculations.

To obtain the free energies of solvation, single-point calculations on the basis of the Priroda-optimized geometries were performed using the ADF 2008.01 code[66-68]. An integration parameter of 6.0 was applied. We have previously found the trends in the structural parameters and molecular properties of the PBE-optimized geometries obtained in the Priroda code to be sufficiently similar to those obtained with the ADF code when using the same functional[52, 69-71]. The solvent effects of pyridine were taken into account with the Conductor-Like Screening Model, COSMO, as implemented in ADF.[72] The Klamt radii were used for the main group atoms (H = 1.30 Å, C = 2.00 Å, N = 1.83 Å and O = 1.72 Å)[73] and for the actinide atom (U = 1.70 Å)[51-53, 74]. The scalar relativistic ZORA method [75-77] was applied in the ADF calculations in conjunction with the PBE functional and triple-ς polarized quality basis sets (ZORA-TZP).

Results and Discussion

Structural Properties. In the case of the reaction of H_4L^2 with one uranyl ion, we designed and optimized the mononuclear complexes $[(UO_2)(H_2L^2)]^{n-2}$ (n = 2 for U^{VI} and n = 1 for U^{V}), Fig. 1. In these complexes, the uranyl group was coordinated to four equatorial nitrogen atoms of the H_2L^2 ligand. The effects of a fifth equatorial ligand on the structures of complexes were also examined by

optimizing the pyridine solvated complexes, $[(UO_2)(py)(H_2L^2)]^{n-2}$ (n = 2 for U^{VI} and n = 1 for U^{V}). The optimized geometries (see selected geometry parameters in Table S1) demonstrate that the four-fold coordination of the uranyl ion in the equatorial plane is reliable and is thus used in the present discussions.

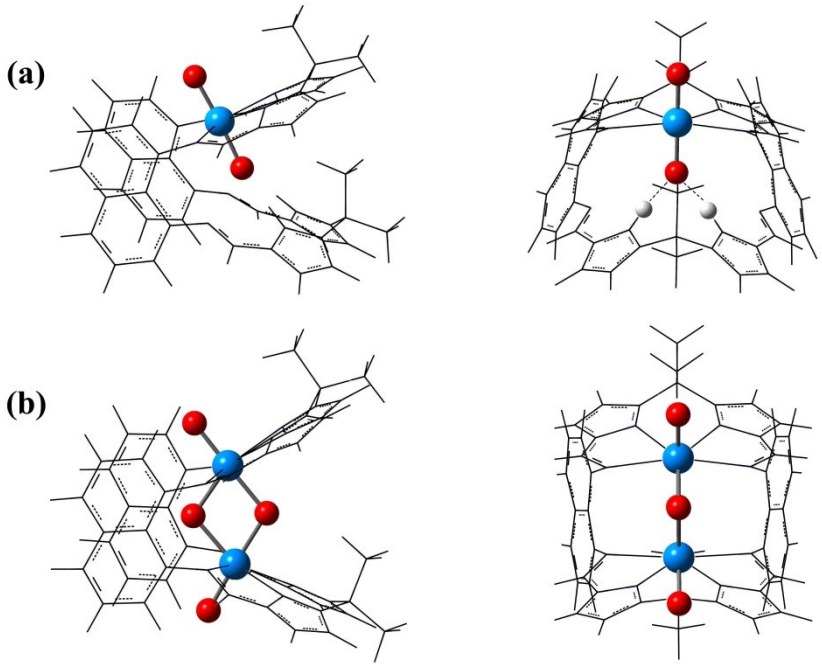


Fig. 1. Structures of (a) mononuclear $[(UO_2)(H_2L^2)]^{n-2}$ and (b) binuclear $[(UO_2)_2(L^2)]^{2n-4}$ (n = 2 for U^{VI}; n = 1 for U^{V}), (left: side-on view, right: face-on view).

The mononuclear uranyl L^2 complexes were calculated to show a Pacman-like[17-19] structure in which one N_4-donor compartment is occupied by one uranyl ion and the second remains vacant. This resembles that of experimentally-known complex $[(UO_2)(THF)(H_2L^1)]$.[9] As shown in Table 2, the U=O bond lengths of the hexavalent complex ($\mathbf{M}^{VI}L^2$) were calculated to be 1.81 and 1.83 Å for *exo*- and *endo*-oxo atoms, respectively. The predicted bond orders of 2.2-2.4 indicate partial triple bonding between the uranium and oxo atoms. The $U{=}O_{endo}$ distance is about 0.02 Å longer than the $U{=}O_{exo}$ bond and originates from two $O_{endo}\cdots$HN(pyrrole) bonding interactions, as shown in Fig. 1. A similar case is also found in the experimentally-reported $[(UO_2)(THF)(L^1)]$ [9] as well as the theoretically-studied $\mathbf{M}^{VI}L^1$ and $\mathbf{M}^{VI}L^3$ (see Fig. S1, Tables S2 and S3.)[53]. Relative to those of the hexavalent complex $\mathbf{M}^{VI}L^2$, the U=O bond distances of pentavalent $\mathbf{M}^{V}L^2$ are lengthened by about

0.03-0.05 Å, Table 2. This elongation of the U=O_{yl} bonds after U(VI)→U(V) reduction is consistent with previous theoretical[78-81] and experimental reports[48, 82-85].

Table 2. Optimized geometry parameters and bond orders (in parentheses) for mononuclear $[(UO_2)(H_2L^2)]^{n-2}$ and binuclear $[(UO_2)_2(L)]^{2n-4}$ (n = 2 for U^{VI}; n = 1 for U^{V}) complexes in the gas phase. (Bond lengths in Å and angles in degree)

Complexes	$\mathbf{M}^{VI}L^2$	$\mathbf{M}^{V}L^2$	$\mathbf{B}^{VI}L^2$	$\mathbf{B}^{V}L^2$
U_1-O_{exo}	1.806 (2.38)	1.835 (2.38)	1.822 (2.44)	1.853 (2.42)
U_1-O_{endo}	1.830 (2.19)	1.882 (2.04)	2.099/2.082 (1.26/1.11)	2.124/2.084 (1.21/1.17)
U_2-O_{exo}			1.819 (2.43)	1.854 (2.41)
U_2-O_{endo}			2.133/2.048 (1.15/1.21)	2.138/2.093 (1.16/1.17)
$O_{endo}\cdots H$	1.942 (0.07)	1.814 (0.12)		
$U_1\cdots U_2$			3.363 (0.32)	3.370 (0.43)
O_{exo}-U_1-O_{endo}	176.6	176.9	176.7/110.4	177.5/108.3
O_{exo}-U_2-O_{endo}			178.9/108.2	178.5/107.8

The unoccupied pyrrole-imine N_4-donor pocket of the L^2 ligand of $\mathbf{M}^{VI}L^2$ may also accommodate another uranyl group, leading to the formation of binuclear uranyl complexes. Full geometry optimizations of $[(U^{VI}O_2)_2(L^2)]$ (labeled as $\mathbf{B}^{VI}L^2$ in Table 1) reveal it as possessing a butterfly-like bis(uranyl) structure as shown in Fig. 1. In this complex, a linear uranyl is coordinated in a side-by-side fashion to a *cis*-uranyl unit. So far, complexes with a parallel structure of two uranyl ions, bridged by oxygen, fluoride and chloride, as well as with T-shaped and diamond-typed structures have been reported,[25, 31, 35, 38, 39] while those with this butterfly-like structure remain rare[24, 86]. In the current case, we find a stable hexavalent bis(uranyl) complex because the special Pacman-like structure of the L^2 ligand facilitates the formation of complex with intramolecular CCIs and, in return, the formed CCIs stablise the hexavalent bis(uranyl) complex. The calculations (Table 2) show that $\mathbf{B}^{VI}L^2$ contains three types of U-O bonds: two short U=O_{exo} bonds of 1.82 Å (mean value), two long U-O_{endo} bonds of 2.07 Å, and two even longer U-O_{endo} bonds of 2.12 Å. Regarding the U-O bond orders, the first group possesses partial triple bond character, whilst the other two groups are singly bonded with some double bond character.

Building on our previous studies[51, 53], we find that the linker size of polypyrrolic ligands strongly affects the geometrical configuration of the bis(uranyl) complex. Regarding binuclear uranium(VI) complexes, the bis(uranyl) ions are ligated by L^1 to form butterfly-like and T-shaped isomers (Fig. 2), where the former is more stable.[51] In contrast, only a butterfly-like complex was predicted to be stable for the L^2, Fig. 1 while the bis(uranyl) complex of L^3 displays a structure (Fig. 2) in which the two linear uranyl ions remain isolated but distorted to limit intramolecular oxo-group interactions.[53] As such, CCIs are found in the L^1 and L^2 complexes, but are absent in the L^3 complex. And the following conclusions can be drawn: (i) L^1 and L^2 contain relatively short linkers that promote stabilising intramolecular uranyl-uranyl CCIs, whereas L^3, with the comparatively long anthracenyl linkers, exploits a lateral twist of the macrocycle to decrease the repulsion between the *endo*-oxo atoms; (ii) L^1 is more flexible than L^2, and allows for expansion of the Pacman cleft to facilitate the formation of a T-shaped complex (Fig. 2b). This is consistent with the experimental results that $[(U^{VI}O_2)(THF)(H_2L^1)]$ can incorporate ions of various sizes such as H, Li and K.[20-23]

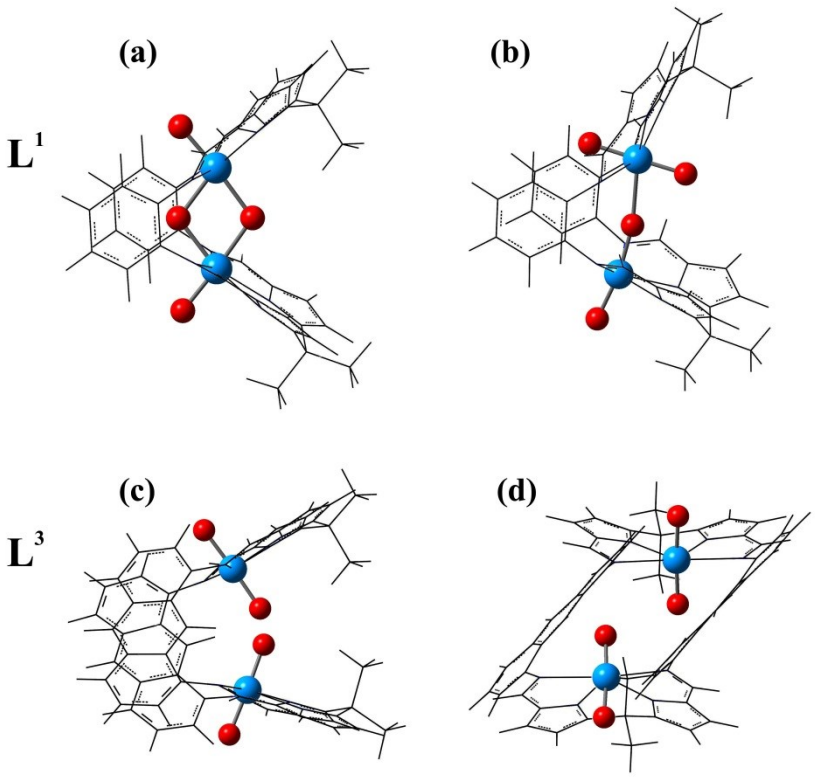


Fig. 2. Structures of the binuclear $[(UO_2)_2(L^x)]^{2n-4}$ ($L^x = L^1$ and L^3) complexes, (a) **B**utterfly-like L^1 isomeric complex, (b) **T**-Shaped L^1 isomeric complex, (c) L^3 complex, side-on view, (d) L^3 complex, face-on view.

Regarding the pentavalent binuclear complexes $[(U^{V}O_2)_2(L)]^{2-}$ (L = L^1, L^2 and L^3), the butterfly-like structure was predicted to be stable for L^1 and L^2, and a bis(uranyl) complex for L^3, Fig. 2. No T-shaped isomer was found to be stable for L^1 at this oxidation state. The binuclear U(V) complexes could adopt either a ferromagnetic triplet or an antiferromagnetic singlet unrestricted electronic state. Our previous study[52] indicated that the calculated geometry parameters, bond orders and atomic charges are very close in these two electronic states. Herein, we only discuss the optimized geometry of $[(U^{V}O_2)_2(L)]^{2-}$ (L = L^1, L^2 and L^3) in the ferromagnetic triplet state. The computed electron-spin densities of the uranium atoms in $\mathbf{B}^{V}L^2$ are 0.98 and 1.04 (Table S6), suggesting about one single electron at each U(V) atom. $\mathbf{B}^{V}L^1$ has quite similar electron-spin densities of the uranium(V) atoms. However, only 0.56 electron spin was found to be located on each U(V) in $\mathbf{N}^{V}L^3$, and the remainder has transferred to the anthracenyl groups of the L^3 ligand.

Binding Energies. Starting from the uranyl complexes of L^1, we used uranyl transfer reactions to examine the possibility of forming the uranyl complexes of L^2 and L^3. As these exchange reactions provide insights into the relative stabilities of the L^2 and L^3 complexes. We note that the uranyl-L^1 complex, $[(U^{VI}O_2)(THF)(H_2L^1)]$, has been synthesized experimentally and characterized,[9] and is a solvated analogue of $\mathbf{M}^{VI}L^1$. The implication of this is that if reactions in Equations 1 and 2 are calculated to be exothermic, then the L^2 and L^3 ligands bind uranyl more strongly than L^1. This suggests then that it should be possible to synthesize the uranyl complexes with these ligands following similar protocols as used for the uranyl-L^1 complex.

$$[(UO_2)(H_2L^1)]^{n-2} + H_4L^x = [(UO_2)(H_2L^x)]^{n-2} + H_4L^1,\ x = 2 \text{ and } 3 \qquad (1)$$

$$[(UO_2)_2(L^1)]^{2n-4} + H_4L^x = [(UO_2)_2(L^x)]^{2n-4} + H_4L^1,\ x = 2 \text{ and } 3 \qquad (2)$$

The reaction energies calculated in the gas phase and pyridine solution are presented in Table 3 and plotted in Fig. 3. In the gas phase, the formation of the $\mathbf{M}^{VI}L^2$ and $\mathbf{M}^{V}L^2$ complexes from their respective L^1 complexes are found to be exothermic. Overall, the calculated energetic driving force ($\Delta_r G$(gas)) of -0.40 and -0.66 kcal/mol are small but less than the endothermic energy requirement of 0.38-2.03 kcal/mol energy for the L^3 complexes. Starting from the bis(uranyl) complexes with the L^1 ligand, the formation of the L^2 and L^3 analogues is endothermic in the gas phase. After incorporation of a solvent environment using the COSMO model, the formation of the L^2 and L^3 complexes were all predicted to be endothermic for both pyridine and water solvents. The most endothermic reaction for the L^2 complexes in pyridine is the formation of the $B^{V}L^2$ complex, 12.70 kcal/mol. We can hypothesise that it should be possible to synthesize experimentally the L^2 complexes in so far as sufficient heat is provided.

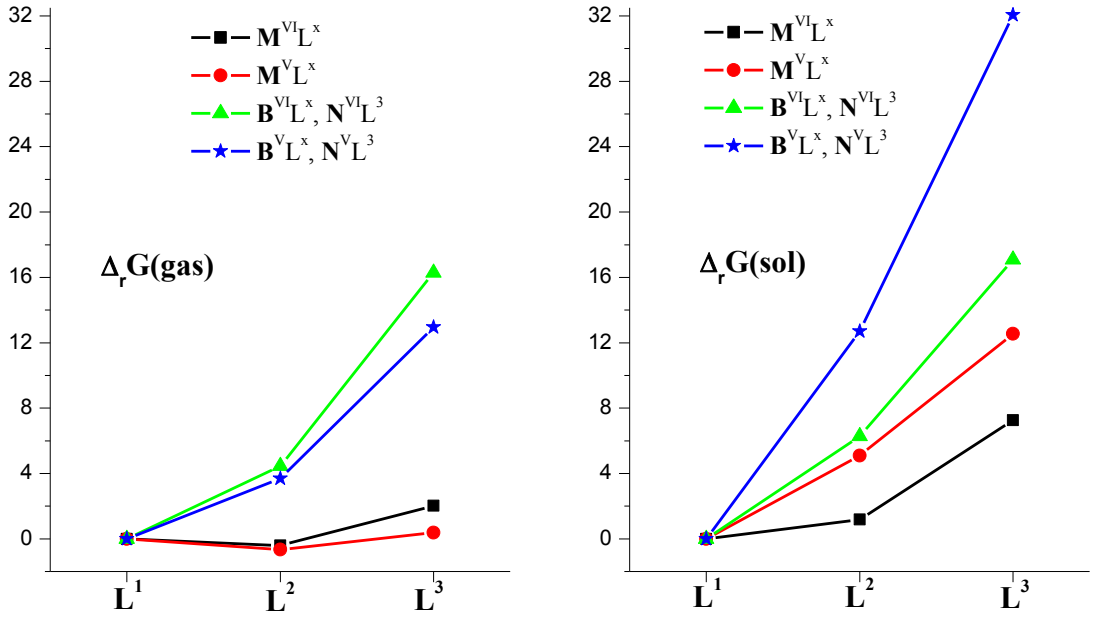


Fig. 3. Free energies (kcal/mol) of uranyl transfer reactions (as seen in Table 3) in the gas phase (left) and pyridine solution (right) for mononuclear $[(UO_2)(H_2L^x)]^{n-2}$ and binuclear $[(UO_2)_2(L^x)]^{2n-4}$ (x = 1, 2 and 3; n = 2 for U^{VI}; n = 1 for U^{V}) complexes.

Table 3. Calculated energies (kcal/mol) of uranyl transfer reactions for mononuclear $[(UO_2)(H_2L^x)]^{n-2}$ and binuclear $[(UO_2)_2(L^x)]^{2n-4}$ (x = 2 and 3; n = 2 for U^{VI}; n = 1 for U^{V}) complexes starting from their respective L^1 complexes.

	Reaction 1: $[(UO_2)(H_2L^1)]^{n-2} + H_4L^x = [(UO_2)(H_2L^x)]^{n-2} + H_4L^1$			
Products	$\Delta_rE(gas)$ [a]	$\Delta_rE_0(gas)$ [a]	$\Delta_rG(gas)$ [a]	$\Delta_rG(sol)$ [a]
$\mathbf{M}^{VI}L^2$	-0.02	-0.43	-0.40	1.18
$\mathbf{M}^{V}L^2$	-1.33	-1.94	-0.66	5.09
$\mathbf{M}^{VI}L^3$	5.48	4.48	2.03	7.25
$\mathbf{M}^{V}L^3$	2.63	1.45	0.38	12.54
	Reaction 2: $[(UO_2)_2(L^1)]^{2n-4} + H_4L^x = [(UO_2)_2(L^x)]^{2n-4} + H_4L^1$			
Products	$\Delta_rE(gas)$	$\Delta_rE_0(gas)$	$\Delta_rG(gas)$	
$\mathbf{B}^{VI}L^2$	3.40	2.92	4.46	6.28
$\mathbf{B}^{V}L^2$	3.53	2.74	3.70	12.70
$\mathbf{N}^{VI}L^3$	16.18	16.03	16.29	17.08
$\mathbf{N}^{V}L^3$	13.96	12.88	12.95	32.05

[a.] $\Delta_rE(gas)$, $\Delta_rE_0(gas)$ and $\Delta_rG(gas)$ denote the total energy, total energy including zero-point vibration energy and free energy of the reaction in the gas phase, respectively. $\Delta_rG(sol)$ corresponds to the free energy of the reaction in the pyridine solution.

Vibrational Spectra. We have simulated the infrared vibrational spectra of the uranyl complexes of L^2 (Fig. 4) using the Lorentz function based on frequency calculations. The absorption bands of $\mathbf{M}^{VI}L^2$ at 774, 796 and 875 cm^{-1} were attributed to the U=O stretching vibrational modes. The first two are symmetric (S) U=O vibrations and the last is an asymmetric (As) one. It is worth pointing out that the absorption peak at 774 cm^{-1} is predominantly a U=O vibration, while more ligand contribution is found in the 796 cm^{-1} band but mixed with a small U=O stretching vibration. In contrast, the $\mathbf{M}^{VI}L^1$ and $\mathbf{M}^{VI}L^3$ analogues exhibit two U=O stretching vibrations at 780 (S) / 888 (As) and 809 (S) / 891 (As) cm^{-1}, respectively (Fig. S2). Additionally, the 674 cm^{-1} band of $\mathbf{M}^{VI}L^2$ has ligand characteristics and the strong absorption at 1003 cm^{-1} is attributable to the U-N vibrations together with further ligand character. As shown in Fig. 4, all of the L^2 complexes show strong similar characteristic absorptions around 1000 cm^{-1}.

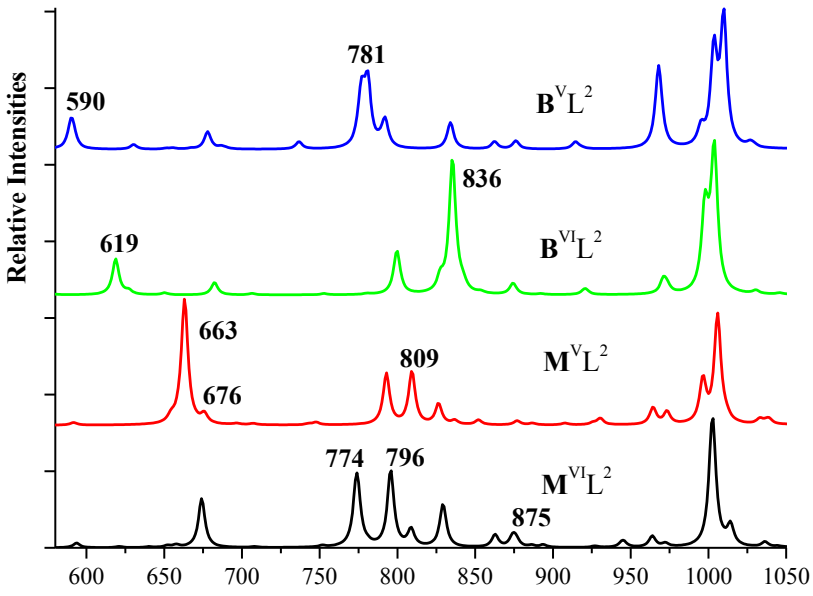


Fig. 4. Simulated vibrational spectra of mononuclear $[(UO_2)(H_2L^2)]^{n-2}$ and binuclear $[(UO_2)_2(L^2)]^{2n-4}$ complexes (n = 2 for U^{VI}; n = 1 for U^{V}). The U-O vibrations were labeled.

For the pentavalent complex $\mathbf{M}^{V}L^{2}$, the U=O stretching vibrations are found at 663 (S), 676 (S) and 809 (As) cm^{-1}, with the symmetric 676 cm^{-1} band very weak (see Fig. 4). The strong perturbation due to the hydrogen bonding between the *endo*-oxo and pyrrolic hydrogens ($H\cdots O_{endo}=U$) results in the very low U=O vibration at 663 cm^{-1} and is similarly seen in the analogous L^{1} and L^{3} complexes, Fig. S3. A low-frequency U=O vibration at 661 cm^{-1} for $\mathbf{M}^{V}L^{1}$ was calculated, close to that at 663 cm^{-1} for $\mathbf{M}^{V}L^{2}$, but is seen at 724 cm^{-1} for $\mathbf{M}^{V}L^{3}$. This difference results from an increased number of hydrogen bonds involved in the L^{1} and L^{2} complexes than in L^{3} complex. The L^{1} and L^{2} complexes contain three types of hydrogen bonds: two strong interactions between the *endo*-oxo atom and two pyrrolic hydrogen atoms in the vacant pocket ($O_{endo}\cdots H$ distances of 1.81-1.86 Å), and one weak interaction with a *meso*-methyl hydrogen (2.47-2.65 Å). In contrast, the L^{3} complex has only two hydrogen bonds: one strong interaction with a pyrrolic hydrogen (1.95 Å) as seen in Fig. S1 and one weak interaction with a *meso*-methyl hydrogen (2.65 Å).

Relative to the mononuclear complexes, the binuclear complexes exhibit strong $U=O_{exo}$ vibrational bands at 836 and 781 cm^{-1} for the $\mathbf{B}^{VI}L^{2}$ and $\mathbf{B}^{V}L^{2}$ complexes respectively (see Fig. 4). With respect to the four-membered ring formed by the uranium and *endo*-oxo atoms, $\mathbf{B}^{VI}L^{2}$ displays four $U\text{-}O_{endo}$ vibrational bands at 269, 544, 489 and 619 cm^{-1}, corresponding to the modes in Chart 2(a-d), respectively; the symmetrical breathing vibration of 619 cm^{-1} has the largest intensity. Similarly, we find four corresponding bands at 287, 391, 488 and 590 cm^{-1} for the pentavalent complex, $\mathbf{B}^{V}L^{2}$. The reduction from U(VI) to U(V) has an apparent effect on vibrational mode (b), resulting in a large red-shift of 153 cm^{-1}. This is related to the $U(V)\text{-}O_{endo}$ bonds of $\mathbf{B}^{V}L^{2}$ being weaker than the $U(VI)\text{-}O_{endo}$ bonds of $\mathbf{B}^{VI}L^{2}$.

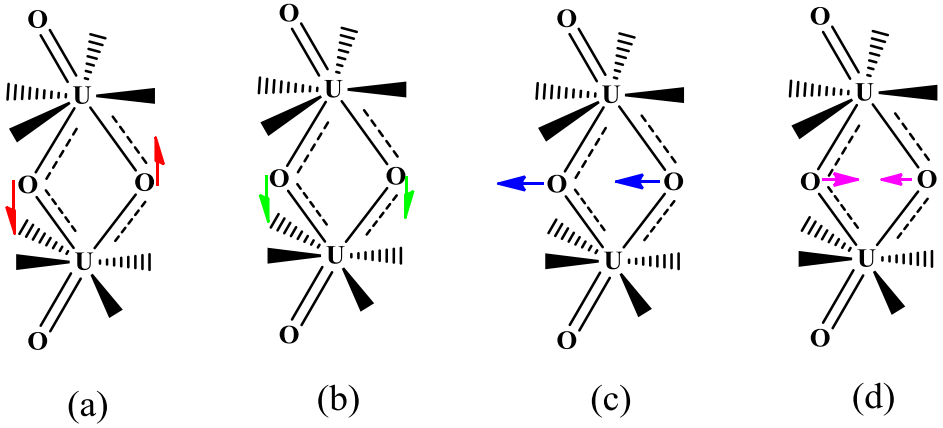


Chart 2. The $U\text{-}O_{endo}$ vibrational modes in the binuclear complexes, $\mathbf{B}^{VI}L^{2}$ and $\mathbf{B}^{V}L^{2}$.

The simulated spectra of the bis(uranyl) complexes of L^1, L^2 and L^3 were also compared and presented in Figs. S2 and S3. It is not difficult to see that the ligands (L^1, L^2 and L^3) have a slight effect on the U=O stretching bands. For instance, 838, 836 and 826 cm^{-1} frequencies were calculated for $\mathbf{B}^{VI}L^1$, $\mathbf{B}^{VI}L^2$ and $\mathbf{N}^{VI}L^3$, respectively, and 776, 781 and 772 cm^{-1} for their corresponding pentavalent analogues. In contrast, the cation-cation interactions make the U=O vibrational peaks of $\mathbf{T}^{VI}L^1$ diversified as seen in. Fig. S2.

Conclusions

In this work, the formation of uranyl and bis(uranyl) complexes by the Schiff-base polypyrrolic macrocycle with naphthalenyl linkers between the N_4-donor compartments (L^2) was examined theoretically using relativistic density functional theory.

It was shown that the mononuclear $\mathbf{M}^{VI}L^2$ and $\mathbf{M}^{V}L^2$ complexes have geometrical configurations similar to that of experimentally-known $[(UO_2)(THF)(H_2L^1)]$.[9] The only stable structure for the binuclear L^2 complexes features a butterfly-like bis(uranyl) core, in which a linear uranyl is coordinated in a side-by-side fashion to a *cis*-uranyl unit. This structure agrees with the recent experimental report of the binuclear complex $[\{(Me_3Si)OU(\mu\text{-}O)\}(L^1)]$ which contains two silylated pentavalent uranium oxo groups derived from two trans-uranyl cations.[24] Associated with our previous studies on L^1 and L^3 complexes[51,53], the hinge size (phenylenyl, naphthalenyl and anthracenyl) of the organic ligands, uranium oxidation states, and intramolecular cation-cation interactions are found to play significant roles in determining the structures of bis(uranyl) complexes.

Frequency calculations provided detailed information about the characteristic bands of the $U\text{-}O_{oxo/endo}$ stretching vibrations. Hexavalent $\mathbf{M}^{VI}L^2$ exhibits the absorption bands in the higher-energy region than pentavalent $\mathbf{M}^{V}L^2$; a low $U{=}O_{endo}$ vibration at 663 cm^{-1} was calculated in $\mathbf{M}^{V}L^2$ due to the strong interaction between the pyrrolic hydrogens and *endo*-oxo atom. The strong $U{=}O_{exo}$ vibrational bands were predicted for the binuclear complexes, while the relative weak $U\text{-}O_{endo}$ vibrational peaks were found in the lower-energy region. Overall, the calculated $U\text{-}O_{oxo/endo}$ stretching vibrational frequencies agree with the trends of their bond orders and bond lengths.

Although the calculated free energies in pyridine solution reveal an endothermic process based on the uranyl transfer reactions starting from L^1 complexes, it should be possible to experimentally synthesize the L^2 complexes using similar protocols employed for the L^1 complexes because the largest energy requirement for the model uranyl transfer reactions is small (< 12.7 kcal/mol).

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